

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representation of  
The original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

**THIS PAGE BLANK (USPTO)**

(15)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(16) Publication number:

**0 264 208  
A2**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 87308729.0

(51) Int. Cl. 4: C08F 8/14

(22) Date of filing: 01.10.87

(30) Priority: 06.10.86 US 915455

(43) Date of publication of application:  
20.04.88 Bulletin 88/16

(86) Designated Contracting States:  
BE DE ES FR GB IT NL

(71) Applicant: ATLANTIC RICHFIELD COMPANY  
515 South Flower Street  
Los Angeles California 90071(US)

(72) Inventor: Le-Khac, BI  
1528 Marlboro Road  
West Chester Pennsylvania 19382(US)

(74) Representative: Cropp, John Anthony David et  
al  
MATHYS & SQUIRE 10 Fleet Street  
London, EC4Y 1AY(GB)

(54) Extended shelf life water-absorbing composition which facilitates fiber formation.

(57) A copolymer of recurring units of at least one  $\alpha, \beta$ -unsaturated monomer and recurring units of at least one copolymerizable comonomer comprising, in its preferred embodiment from about 20 to about 80 percent pendant carboxylic acid units and from about 80 to about 20 percent pendant carboxylate salt units, is blended with at least one monomer containing at least two hydroxyl groups to produce a water-absorbing composition upon curing. The composition is particularly suitable for fiber formation.

EP 0 264 208 A2

This invention relates to water-absorbing compositions.

In one of its more specific aspects, this invention relates to the incorporation of water-absorbing compositions into articles of manufacture for the purpose of improving the absorbent properties of the articles.

50 Absorbent compositions are widely used in the manufacture of products which require high absorption capability. For example, water-absorbing compositions are used in the manufacture of surgical and dental sponges, tampons, sanitary napkins and pads, bandages, disposable diapers, meat trays, and household pet litter. Water-absorbing compositions are also used for the modification of soil to improve water retention and increase air capacity and for a host of other applications.

10 As used herein, the term "water" when used in the phrases "water-absorbing" and "water-absorbent" is understood to mean not only water but also electrolyte solutions such as body fluids.

A number of absorbent compositions have been developed which exhibit water absorption capacity. For example, U.S. Pat. Nos. 3,954,721 and 3,983,095 disclose preparations for derivatives of copolymers of maleic anhydride with at least one suitable vinyl monomer in fibrous form. The fibrous copolymers are  
15 rendered hydrophilic and water-swellaable by reaction with ammonia or an alkali metal hydroxide. U.S. Pat. No. 3,810,468 discloses lightly cross-linked olefin-maleic anhydride copolymers prepared as substantially linear copolymers and then reacted with a diol or a diamine to introduce cross-linking. The resultant lightly cross-linked copolymers are treated with ammonia or an aqueous or alcohol solution of an alkali metal hydroxide. U.S. Pat. No. 3,989,586 describes the preparation of sorptive paper products by incorporating  
20 cross-linked copolymers of styrene or olefins with maleic anhydride in a paper web which is then treated to convert the copolymer to a water-swellaable salt form. U.S. Pat. No. 3,980,663 describes water-swellaable absorbent articles made from carboxylic polyelectrolytes via cross-linking with glycerine diglycidyl ether. U.S. Pat. Nos. 4,332,917 and 4,338,417 disclose blends of copolymers of styrene and maleic anhydride with polymers derived from a monomeric ester having vinyl unsaturation e.g., poly(vinyl acetate), cellulose triacetate, cellulose aceto-butylate, poly(ethylacrylate) and poly(methylmethacrylate). U.S. Pat. No.  
25 4,420,588 teaches a water absorbing rubber composition comprising a 1,3-diene rubber and a water-absorbing resin dispersed in the rubber.

The desirability of having water-absorbing compositions in fibrous forms is well known. For example, in sanitary products such as disposable diapers and tampons, fibers can be more easily confined within the  
30 product. In this respect, the prior art water-absorbing compositions are deficient; they do not facilitate fiber formation. Because of the speed of their crosslinking reactions, the prior art water-absorbing compositions possess no appreciable shelf life; fiber formation must be completed shortly after the compositions are prepared. This shelf life deficiency in the prior art compositions is discussed in U.S. Pat. No. 3,983,095 which teaches that fiber formation should be completed within several hours and in some cases immediately, depending upon the reactivity of the cross-linking agent used.  
35

The water-absorbing compositions of this invention possess excellent shelf life and have been found suitable for forming into fibers several months after preparation. They facilitate fiber formation over a wide range of time and temperature. They also possess excellent integrity in the hydrogel or water-swollen state, exhibit excellent water and electrolyte solution absorption capacity, and are readily incorporated into  
40 conventional water-absorbing products using conventional methods.

According to this invention there is provided a composition which is water-absorbent upon curing comprising (a) a copolymer containing from about 25 to about 75 mole percent of at least one  $\alpha,\beta$ -unsaturated monomer bearing at least one pendant unit selected from the group consisting of carboxylic acid units and derivatives of carboxylic acid units and from about 75 to about 25 mole percent of at least  
45 one copolymerizable comonomer, wherein from about 20 to about 80 percent of the total pendant units introduced through the  $\alpha,\beta$ -unsaturated monomer are carboxylic acid units or must be converted into carboxylic acid units, and wherein from about 80 to about 20 percent of the total pendant units are carboxylate metal salt units or must be converted into carboxylate salt units; and (b) at least one monomer containing at least two hydroxyl groups selected from the group consisting of: alkylene glycols containing 2-  
50 10 carbon atoms and their ethers; cycloalkylene glycols; Bisphenol A; hydroxy alkylene derivatives of Bisphenol A; hydroquinone; phloroglucinol; hydroxy alkylene derivatives of diphenols; glycerol; erythritol; pentaerythritol; and all natural monosaccharides.

According to this invention there is provided a method of producing a water-absorbing composition comprising the steps of: (a) preparing a blend of i) a copolymer containing from about 25 to about 75 mole  
55 percent recurring units of at least one  $\alpha,\beta$ -unsaturated monomer which bears at least one pendant unit selected from the group consisting of carboxylic acid units and derivatives of carboxylic acid units, and from about 75 to 25 mole percent recurring units of at least one copolymerizable comonomer, wherein from about 20 to about 80 mole percent of the total pendant units introduced through the recurring  $\alpha,\beta$ -

unsaturated monomer units are carboxylic acid units or must be converted into carboxylic acid units and wherein from about 80 to about 20 percent of the total pendant units are carboxylate salt units or must be converted into carboxylate salt units; and ii) at least one monomer containing at least two hydroxyl groups selected from the group consisting of: alkylene glycols containing 2-10 carbon atoms and their ethers; cycloalkylene glycols; Bisphenol A; hydroxy alkylene derivatives of Bisphenol A; hydroquinone; phloroglucinol; hydroxy alkylene derivatives of diphenols; glycerol; erythritol; pentaerythritol; and all natural monosaccharides; and (b) curing the resulting blend.

According to this invention there is provided a method of absorbing water and electrolyte solutions comprising the step of contacting the water or electrolyte solution to be absorbed with a cured water absorbing composition comprising a blend of: (a) a copolymer containing from about 25 to about 75 mole percent of at least one  $\alpha,\beta$ -unsaturated monomer bearing at least one pendant unit selected from the group consisting of carboxylic acid units and derivatives of carboxylic acid units and from about 75 to 25 mole percent of at least one copolymerizable comonomer, wherein from about 20 to about 80 percent of the total pendant units introduced through the  $\alpha,\beta$ -unsaturated monomer are carboxylic acid units or must be converted into carboxylic acid units, and wherein from about 80 to about 20 percent of the total pendant units are carboxylate salt units or must be converted into carboxylate salt units; and (b) at least one monomer containing at least two hydroxyl groups selected from the group consisting of: alkylene glycols containing 2-10 carbon atoms and their ethers; cycloalkylene glycols; Bisphenol A; hydroxy alkylene derivatives of Bisphenol A; hydroquinone; phloroglucinol; hydroxy alkylene derivatives of diphenols; glycerol; erythritol; pentaerythritol; and all natural monosaccharides.

An article of manufacture comprising a cured water-absorbing composition and a means for supporting said composition to present said composition for absorption usage, wherein said water-absorbing composition comprises a blend of: (a) a copolymer containing from about 25 to about 75 mole percent of at least one  $\alpha,\beta$ -unsaturated monomer bearing at least one pendant unit selected from the group consisting of carboxylic acid units and derivatives of carboxylic acid units and from about 75 to about 25 mole percent of at least one copolymerizable comonomer, wherein from about 20 to 80 percent of the total pendant units introduced through the  $\alpha,\beta$ -unsaturated monomer are carboxylic acid units or must be converted into carboxylic acid units, and wherein from about 80 to about 20 percent of the total pendant units are carboxylate salt units or must be converted into carboxylate salt units; and (b) at least one monomer containing at least two hydroxyl groups selected from the group consisting of: alkylene glycols containing 2-10 carbon atoms and their ethers; cycloalkylene glycols; Bisphenol A; hydroxy alkylene derivatives of Bisphenol A; hydroquinone; phloroglucinol; hydroxy alkylene derivatives of diphenols; glycerol; erythritol; pentaerythritol; and all natural monosaccharides.

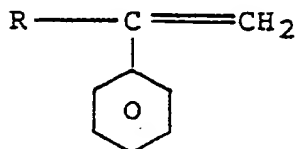
According to this invention there is also provided a method of enhancing at least one water absorbing characteristic of an article which method comprises the step of incorporating into the article a cured water-absorbing composition comprising a blend of: (a) a copolymer containing from about 25 to about 75 mole percent of at least one  $\alpha,\beta$ -unsaturated monomer bearing at least one pendant unit selected from the group consisting of carboxylic acid units and derivatives of carboxylic acid units and from about 75 to about 25 mole percent of at least one copolymerizable comonomer, wherein from about 20 to about 80 percent of the total pendant units introduced through the  $\alpha,\beta$ -unsaturated monomer are carboxylic acid units or must be converted into carboxylic acid units, and wherein from about 80 to about 20 percent of the total pendant units are carboxylate salt units or must be converted into carboxylate metal salt units; and (b) at least one monomer containing at least two hydroxyl groups selected from the group consisting of: alkylene glycols containing 2-10 carbon atoms and their ethers; cycloalkylene glycols; Bisphenol A; hydroxy alkylene derivatives of Bisphenol A; hydroquinone; phloroglucinol; hydroxy alkylene derivatives of diphenols; glycerol; erythritol; pentaerythritol; and all natural monosaccharides, said composition being incorporated into the article in an effective amount to enhance at least one waterabsorbing characteristic of the article as compared to the water-absorbing characteristics of the article in the absence of the composition.

Copolymers suitable for use to produce water-absorbing compositions of the invention will contain from about 25 to about 75 total mole percent recurring units of at least one  $\alpha,\beta$ -unsaturated monomer and from about 75 to about 25 total mole percent recurring units of at least one copolymerizable comonomer. Preferably, the copolymer will contain from about 35 to about 65 total mole percent of recurring units of at least one  $\alpha,\beta$ -unsaturated monomer and from about 65 to about 35 total mole percent of at least one copolymerizable comonomer. Most preferably, the copolymer will be an equimolar copolymer.

Suitable  $\alpha,\beta$ -unsaturated monomers are those bearing at least one pendant carboxylic acid unit or derivative of a carboxylic acid unit. Derivatives of carboxylic acid units include carboxylic acid salt groups, carboxylic acid amide groups, carboxylic acid imide groups, carboxylic acid anhydride groups and carboxylic acid ester groups.

Suitable  $\alpha,\beta$  -unsaturated monomers include maleic acid; crotonic acid; fumaric acid; mesaconic acid; the sodium salt of maleic acid; the sodium salt of 2-methyl, 2-butene dicarboxylic acid; the sodium salt of itaconic acid; maleamic acid; maleamide; N-phenyl maleimide; maleimide; maleic anhydride; fuameric anhydride; itaconic anhydride; citraconic anhydride; mesaconic anhydride; methyl itaconic anhydride; ethyl maleic anhydride; diethylmaleate; methylmaleate; and the like, and their mixtures.

Any suitable copolymerizable comonomer can be employed. Suitable copolymerizable comonomers include ethylene, propylene, isobutylene,  $C_1$  to  $C_4$  alkyl methacrylates, vinyl acetate, methyl vinyl ether, isobutyl vinyl ether, and styrenic compounds having the formula:



wherein R represents hydrogen or an alkyl group having from 1 to 6 carbon atoms and wherein the benzene ring may be substituted with low molecular weight alkyl or hydroxy groups.

Suitable  $C_1$  to  $C_4$  alkyl acrylates include methyl acrylate, ethyl acrylate, isopropyl acrylate, n-propyl acrylate, n-butyl acrylate, and the like, and their mixtures.

Suitable  $C_1$  to  $C_4$  alkyl methacrylates include methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, n-propylmethacrylate, n-butyl methacrylate, and the like, and their mixtures.

And, suitable styrenic compounds include styrene,  $\alpha$ -methylstyrene, p-methylstyrene, t-butyl styrene, and the like, and their mixtures.

The pendant units on the  $\alpha,\beta$ -unsaturated monomer, will determine what, if any, additional reactions must be carried out to obtain a copolymer having the requisite pendant units necessary to produce the water-absorbing compositions of this invention, that is about 20 to about 80 percent pendant carboxylic acid units and about 80 to about 20 percent pendant carboxylate salt units. Preferably, both units are present in an amount of from about 30 to about 70 percent.

In general, if the  $\alpha,\beta$  -unsaturated monomer bears only carboxylic acid amide, carboxylic acid imide, carboxylic acid anhydride, carboxylic acid ester groups, or mixtures thereof, it will be necessary to convert at least a portion of such carboxylic acid derivative groups to carboxylic acid groups by, for example, a hydrolysis reaction. If the  $\alpha,\beta$  -unsaturated monomer bears only carboxylic acid salt groups, acidification to form carboxylic acid groups will be necessary.

Similarly, the final copolymer must contain from about 80 to 20 percent pendant carboxylate salt units. Accordingly, it may be necessary to carry out a neutralization reaction. Neutralization of carboxylic acid groups with a strong organic or inorganic base such as NaOH, KOH, ammonia, ammonia-in-water solution, or organic amines will result in the formation of carboxylate salt units, preferably carboxylate metal salt units.

Moreover, the sequence and the number of reactions (hydrolysis, acidification, neutralization, etc.) carried out to obtain the desired functionality attached to copolymer backbone are not critical. Any number and sequence resulting in a final copolymer which possesses from about 20 to about 80 percent pendant carboxylic acid units and from about 80 to about 20 percent pendant carboxylate salt units is suitable.

One copolymer particularly suitable for use is a copolymer of maleic anhydride and isobutylene.

Another is maleic anhydride and styrene. Suitable copolymers will have peak molecular weights of from about 5,000 to about 500,000 or more.

Suitable copolymers of maleic anhydride and isobutylene can be prepared using any suitable conventional method. Such copolymers are also commercially available from Kuraray Isoprene Chemical Company, Ltd., Tokyo, Japan, under the trademark ISOBAM. ISOBAM copolymers are available in several grades which are differentiated by viscosity molecular weight: ISOBAM-10, 160,000 to 170,000; ISOBAM-06, 80,000 to 90,000; ISOBAM-04, 55,000 to 65,000; and ISOBAM-600, 6,000 to 10,000.

To produce a water-absorbing composition of this invention, at least one copolymer as described above and at least one monomer bearing at least two hydroxyl groups are blended such that the water-absorbing composition contains in weight percent, from about 80 to about 99.5 total copolymer and from about 0.5 to about 20 total monomer. Preferably, the composition will contain from about 90 to about 99 weight percent total copolymer and from about 1 to about 10 weight percent total monomer.

Any suitable monomer bearing at least two hydroxyl groups and having a relatively low molecular weight, less than 1,000, can be employed in the practice of this invention.

Suitable monomers include ethylene glycol, propylene glycol, trimethylene glycol, 1,4-butane diol, 2-methyl 1,3-propane diol, neopentyl glycol, 1,5-pentane diol, diethylene glycol, dipropylene glycol, 1,4-cyclohexane dimethanol, Bisphenol A, 1,4-bis-( $\beta$ -hydroxyethoxy)bisphenol, hydroquinone, phloroglucinol, glycerol, erythritol, pentaerythritol, 1,7-dihydroxysedoheptulose, and the like.

5 Particularly suitable monomers for use in the practice of this invention are ethylene glycol, propylene glycol, 1,4-butane diol, diethylene glycol, and glycerol. A mixture of two or more of these may be used. Particularly preferred is a combination of 1,4-butane diol and pentaerythritol.

The water-absorbing composition of this invention can be prepared using any suitable blending method such as described in the examples which follow. After the water-absorbing composition is prepared, but  
10 typically before it is cured but some instances as it is curing, it is processed into any desired form using conventional methods of fabrication. For example, the water-absorbing composition can be subjected to casting; spray drying; air-assisted spray drying; air attenuation; wet, dry or flash spinning; and the like. The selection of the process is typically dictated by the shape or form needed for end use. Forms that the water-absorbing composition may be fabricated into include films or sheets, powders and granules, fibers  
15 and any form into which fibers can be processed such as for example milled fibers, chopped fibers, fluff or bulk fibers, strands, yarns, woven fabrics, non-woven mats and the like using a variety of methods, including twisting, beaming, slashing, warping, quilling, severing, texturizing, weaving, knitting, braiding etc.

While not meaning to be limited to any theory, the monomer bearing at least two hydroxyl groups is believed to serve as a high temperature, slow-reacting, cross-linking type agent for the copolymer particles  
20 resulting in the formation of covalent cross-link type bonds upon curing. For example, it has been found that, if a partially neutralized styrene-maleic anhydride copolymer is blended with propylene glycol to form a water-absorbing composition according to this invention, a temperature about 150°C. or higher is typically required to achieve cure. Similarly, if a partially neutralized ethylenemaleic anhydride copolymer is employed, a temperature of 140°C. or higher is typically needed to achieve cure. And, if a partially  
25 neutralized isobutylene-maleic anhydride copolymer is employed, a temperature of 200°C. or higher is typically needed to achieve cure.

Without meaning to limit the invention, the water-absorbing compositions of this invention are particularly well suited for being made into fibers because of the wide time and temperature ranges over which they can be shaped. More specifically, the water-absorbing compositions of this invention can be formulated  
30 to cure at temperatures within the range of from about 140°C to about 250°C. or higher and possess shelf lives in excess of two months as demonstrated in Example 7. Hence, the water-absorbing compositions of this invention can be easily made into fibers using conventional fiber-forming methods and equipment. Moreover, no post-treatment (e.g., a salt-forming reaction as taught in U.S. Patent 3,983,095) of the cured fiber products is required.

35 The water-absorbing compositions of this invention and articles of manufacture into which the compositions are incorporated are suitable for use in a wide range of absorptive functions. In general, the articles into which the water-absorbing compositions are incorporated serve the function of supporting the composition and presenting it in a form adapted for absorptive end use. Means to support and present the composition for absorptive use include, but are not meant to be limited to bandages, surgical and dental  
40 sponges, tampons, sanitary napkins and pads, disposable diapers, meat trays, pads for absorption of perspiration, and the like.

In one embodiment, a water-absorbing composition of this invention is incorporated into a disposable diaper, using conventional fabrication methods to form a diaper composite having the following typical layers: (1) an outer layer (away from the body) of impermeable polyethylene film; (2) a first cellulosic pulp  
45 layer superimposed on the film; (3) a layer of (i) a cured water-absorbing composition of this invention in the form of, for example, fluff, a fibrous mass, a non-woven fiber mat or a woven fabric; or (ii) a layer comprising a blend of a cured water-absorbing composition of this invention and another fluff conventionally employed in diapers; (4) an optional, second cellulosic pulp layer; and (5) an inner permeable polyethylene film layer.

50 Fibers made from the water-absorbing compositions of this invention are particularly suitable for absorbent applications. It is well known that a mass of fibers provides a large surface area for contact with the liquid material to be absorbed. Fibers as compared to powders can also be more easily confined within the article into which they are incorporated.

The following examples serve to further demonstrate the invention.

55

- Using substantially the procedure of Example 1, about 226.13 g of the aqueous solution of the partially neutralized isobutylene/maleic anhydride copolymer produced in Example 1 were mixed with about 2.19 g of ethylene glycol and concentrated to give a 45% solids composition (Composition V) containing 3 phr of ethylene glycol based on the weight of the isobutylene/maleic anhydride copolymer. About 20-25 micron diameter fibers were prepared from the composition as described in Example 1. The absorbency of the fibers and the effect of three different cure temperatures, 190°C., 200°C., and 210°C. on samples of the fibers are shown in following Table 3.

TABLE 3

Composition	V	V	V
Cure Temperature (°C.)	190	200	210
Swell Index			
• Atmospheric Pressure	39.9	37.2	32.5
• 0.5 psi	25.5	24.5	20.1
% Solubility	15.9	11.4	7.7

## EXAMPLE 3

This example demonstrates the preparation of a water-absorbing composition of this invention using ISOBAM 10 isobutylene/maleic anhydride copolymer and 1,4-butane diol. Fibers produced from the composition were cured at different temperatures and the effect of curing at different temperatures is shown in Table 4.

Using substantially the procedure of Example 1, about 150.07 g of the aqueous solution of the partially neutralized isobutylene/maleic anhydride copolymer produced in Example 1 were mixed with about 3.39 g of 1,4-butane diol and concentrated to give a 45% solids composition (Composition VI) containing 7 phr of 1,4-butane diol based on the weight of the isobutylene/maleic anhydride copolymer. About 5-10 micron diameter fibers were prepared from the composition as described in Example 1. The absorbency of the fibers and the effect of three different cure temperatures, 170°C., 180°C., and 190°C. on samples of the fibers are shown in following Table 4.

TABLE 4

Fibers of Composition	VI	VI	VI
Cure Temperature (°C.)	170	180	190
Swell Index			
• Atmospheric Pressure	39.4	36.4	27.5
• 0.5 psi	25.9	23.5	16.2
% Solubility	15.1	8.0	5.4



EXAMPLE 4

This example demonstrates the preparation of different diameter fibers from a water-absorbing composition of this invention and shows the effect of fiber diameter on the absorbency of fibers of the same composition (Composition VII). Substantially the same materials and procedures of Example 1 were employed.

About 1270 g of isobutylene/maleic anhydride copolymer and about 2007 g of demineralized water were added to a mixing vessel with stirring and heated to about 90°C. About 658.3 g of a 50% sodium hydroxide solution were added slowly over a one hour period. The reactor contents were stirred for about one hour, and then about 88.96 g (7 phr) of propylene glycol were added to the reactor. The reactor contents were stirred for about 9 hours at 90°C.

A vacuum pump equipped with a cold trap was hooked to the top of the mixing vessel and excess water was removed to yield an aqueous solution having a solids content of about 55%.

The 55% solids solution was charged into a holding tank equipped with two 0.020" nozzles located at the bottom of the tank. The solution was extruded through the nozzles under pressure into fibers which were wound onto a take-off roller. Fibers of different diameters were prepared by changing the speed of the take-off rollers and thus the speed at which fibers were drawn.

Four different diameter fibers were produced and cured at 210°C. for about 30 minutes. The absorbency of the fibers and the effect of fiber diameter on the absorbency of the fibers are shown in Table 5.

TABLE 5

Fibers of Composition	VII	VII	VII	VII
Fiber Diameter (microns)	10	25	100	175
Swell Index				
• Atmospheric Pressure	33.0	33.8	46.5	50.8
• 0.5 psi	25.0	22.2	30.2	35.0
% Solubility	14.1	15.2	7.2	11.9

EXAMPLE 5

This example demonstrates the preparation of a water-absorbing composition of this invention using ISOBAM 10 isobutylene/maleic anhydride copolymer and glycerol. Fibers produced from the composition (Composition VIII) were cured at two different temperatures, and the effect of the different cure temperatures is shown in Table 6.

Using substantially the procedure of Example 1, about 2869 g of the aqueous solution of the partially neutralized isobutylene/maleic anhydride copolymer of Example 1 were mixed with 64.8 g of glycerol and concentrated to give a 45% solids composition containing 7 phr glycerol based on the weight of the isobutylene/maleic anhydride copolymer. Samples of fibers having diameters of about 10 microns were produced by dry spinning and separately cured at 170°C. and 180°C. for 30 minutes and tested for absorbency. The test results are shown in Table 6.

TABLE 6

5	Fibers of Composition	VIII	VIII
	Cure Temperature (°C.)	170	180
10	Swell Index		
	• Atmospheric Pressure	43.8	34.2
	• 0.5 psi	28.3	24.9
15	% Solubility	16.7	11.7

EXAMPLE 6

20 This example demonstrates the preparation of a water-absorbing composition of this invention using ISOBAM 10 isobutylene/maleic anhydride copolymer and diethylene glycol. Fibers produced from the composition (Composition IX) were cured at two different temperatures, and the effect of the different cure temperatures is shown in Table 7.

25 Using substantially the procedure of Example 1, about 109.22 g of the aqueous solution of the partially neutralized isobutylene/maleic anhydride copolymer of Example 1 were mixed with 2.47 g of diethylene glycol and concentrated to give a 45% solids composition containing 7 phr diethylene glycol based on the weight of the isobutylene/maleic anhydride copolymer. Samples of fibers having diameters of about 10-20 microns were produced by dry spinning and separately cured at 170°C. and 180°C. for 30 minutes and tested for absorbency. The test results are shown in Table 7.

30

TABLE 7

35	Fibers of Composition	IX	IX
	Cure Temperature (°C.)	170	180
40	Swell Index		
	• Atmospheric Pressure	58.8	38.3
	• 0.5 psi	41.3	32.9
45	% Solubility	21.6	12.7

EXAMPLE 7

50 This example demonstrates that the water-absorbing compositions of this invention possess excellent shelf-life in solution form.

A sample of the aqueous solution prepared according to the procedure of Example 5 was aged at 90°C in a closed container. Solution viscosity measurements using a Brookfield viscometer were taken after 6, 29, 35 and 41 hours aging. The viscosities measured are listed in Table 8, below. After 41 hours no gel formation was observed in the solution.

55

TABLE 8

5	Composition (aqueous solution)	VIII
	<u>Aging Time at 90°C</u>	<u>Viscosity (Poises)</u>
10	0 hr	700
	6 hrs	773
	29 hrs	802
15	35 hrs	757
	41 hrs	776

20 Another sample of the aqueous solution of Example 5 was aged for 11 weeks at ambient temperature. After 11 weeks aging, fibers were prepared from the aged solution and the resulting fibers were cured at 180°C for 30 minutes.

25 The absorbent property data of the resulting fibers prepared after 11 weeks compared with the absorbent property data of the fibers produced from the same composition (Example 5) but in the absence of aging, the composition is shown in Table 9.

TABLE 9

30	Fiber of Composition	VIII	VIII
	Time of Solution Aging	0	11 weeks
35	Swell Index:		
	• Atmospheric Pressure	34.2	41.2
40	• 0.5 psi	24.9	30.3

45 The above data demonstrate that fibers of the invention produced after eleven weeks aging from the composition of Example 5 do not lose their absorbent properties as compared to the absorbent properties of fibers prepared in the absence of aging.

It will be evident from the foregoing that various modifications can be made to this invention. Such, however, are considered as being within the scope of the invention.

50

**Claims**

1. A composition which is water-absorbent upon curing comprising:

55 a) a copolymer containing from about 25 to about 75 mole percent recurring units of at least one  $\alpha,\beta$ -unsaturated monomer bearing at least one pendant unit selected from the group consisting of carboxylic acid units and derivatives of carboxylic acid units and from about 75 to about 25 mole percent recurring units of at least one copolymerizable comonomer, wherein from about 20 to about 80 percent of the total pendant units introduced through the recurring units of the  $\alpha,\beta$ -unsaturated monomer must either be

carboxylic acid units or must be converted into carboxylic acid units, and wherein from about 80 to 20 percent of the total pendant units must either be carboxylate salt units or must be converted into carboxylate salt units; and

- b) at least one monomer containing at least two hydroxyl groups selected from the group consisting of: alkylene glycols containing 2-10 carbon atoms and their ethers; cycloalkylene glycols; Bisphenol A, hydroxy alkylene derivatives of Bisphenol A, hydroquinone; phloroglucinol; hydroxy alkylene derivatives of diphenols; glycerol, erythritol, pentaerythritol, and all natural monosaccharides.

2. A composition as claimed in claim 1 which said copolymer contains from about 35 to about 65 mole percent recurring units of said at least one  $\alpha, \beta$ -unsaturated monomer and from about 65 to about 35 mole percent of said at least one copolymerizable comonomer and preferably is an equimolar copolymer.

3. A composition as claimed in claim 1 or 2 comprising in weight percent from about 80 to about 99.5 of said copolymer and from about 0.5 to about 20 of said monomer bearing at least two hydroxyl groups, and preferably from about 90 to 99 of said copolymer and from about 1 to about 10 of said monomer bearing at least two hydroxyl groups.

4. A composition as claimed in any one of claims 1 to 3 in which said copolymer is selected from copolymers of styrene and maleic anhydride, copolymers of ethylene and maleic anhydride, and copolymers of isobutylene and maleic anhydride.

5. A composition as claimed in any one claims 1 to 4 in which said monomer is selected from ethylene glycol, propylene glycol, 1,4-butane diol, diethylene glycol, glycerol, and pentaerythritol and mixtures of two or more thereof, preferably 1,4-butane diol and pentaerythritol.

6. A method of producing a water-absorbing composition comprising the steps of:

- a) forming a composition as claimed in any one of claims 1 to 5, and
- b) curing said composition.

7. A method as claimed in claim 6 comprising the step of forming the composition into a shaped article after the composition is prepared but before it is fully cured.

8. A method as claimed in claim 7 in which the shaped article is selected from fibers, powder and film.

9. A method as claimed in any one of claims 6 to 8 in which said curing is induced by heating the composition.

10. An article of manufacture comprising a cured water-absorbing composition as claimed in any one claims 1 to 5, or formed by the method claimed in any one of claims 6 to 9, and a means for supporting said composition for absorption usage.

11. An article as claimed in claim 10 in which said means for supporting said composition is selected from disposable diapers, tampons, sanitary napkins, surgical and dental sponges and bandages.

12. An article as claimed in claim 10 or claim 11 in which said composition is incorporated into said means for supporting in a fibrous form, in the form of powder, or in the form of film.

13. A method of enhancing the water absorption characteristics of an article of manufacture which comprises the step of incorporating into said article a cured water absorbing composition when said composition is: a composition as claimed in any one of claims 1 to 5 or said cured composition has been obtained by the method claimed in any one of claims 6 to 9 said composition being incorporated into said article in an effective amount to enhance at least one water-absorbing characteristic of said article as compared to the water-absorbing characteristics of the article in the absence of the composition.

14. A method as claimed in claim 13 in which said article of manufacture is selected from disposable diapers, tampons, sanitary napkins and disposable bandages.

15. A method as claimed in claim 13 or claim 14 in which said composition is incorporated into said means for supporting in a fibrous form, in the form of powder, or in the form of film.

16. A method of absorbing water and electrolyte solutions comprising the step of contacting the water or electrolyte solution to be absorbed with a cured water-absorbing composition wherein said composition is a composition as claimed in any one of claims 1 to 5 or said cured composition is obtained by the method of any one of claims 6 to 9.

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 264 208**  
**A3**

(12)

# EUROPEAN PATENT APPLICATION

(21) Application number: 87308729.0

(51) Int. Cl.4: C08F 8/14

(22) Date of filing: 01.10.87

(30) Priority: 06.10.86 US 915455

(43) Date of publication of application:  
20.04.88 Bulletin 88/16(64) Designated Contracting States:  
BE DE ES FR GB IT NL(68) Date of deferred publication of the search report:  
31.05.89 Bulletin 89/22

(71) Applicant: ARCO CHEMICAL TECHNOLOGY  
INC.  
3 Christina Centre Suite 902 201 N Walnut  
Street  
Wilmington Delaware 19801(US)

(72) Inventor: Le-Khac, BI  
1528 Marlboro Road  
West Chester Pennsylvania 19382(US)

(74) Representative: Cropp, John Anthony David et  
al  
MATHYS & SQUIRE 10 Fleet Street  
London, EC4Y 1AY(GB)

(54) Extended shelf life water-absorbing composition which facilitates fiber formation.

(57) A copolymer of recurring units of at least one  $\alpha,\beta$ -unsaturated monomer and recurring units of at least one copolymerizable comonomer comprising, in its preferred embodiment from about 20 to about 80 percent pendant carboxylic acid units and from about 80 to about 20 percent pendant carboxylate salt units, is blended with at least one monomer containing at least two hydroxyl groups to produce a water-absorbing composition upon curing. The composition is particularly suitable for fiber formation.

EP 0 264 208 A3



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 87 30 8729

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	GB-A-2 126 591 (KAO) * Claims; page 2, lines 6-12; page 3, lines 19,38-43 *	1-3,5,6 ,9-16	C 08 F 8/14
X	FR-A-2 525 121 (NIPPON SHOKUBAI) * Claims 1,2,4,5; page 6, lines 13-19; example 1 *	1-3,5,6 ,8-16	
X	GB-A-1 085 047 (ÖSTERREICHISCHE STICKSTOFFWERKE AG) * Claims *	1-6	
X	US-A-2 418 688 (F.C. ATWOOD) * Claim *	1-6	
X	US-A-3 085 986 (I.E. MUSKAT) * Claims *	1-6	
X	US-A-3 933 747 (R.M. NOWAK) * Claims; column 1, line 67 - column 2, line 10; column 2, lines 30-32 *	1-6	
X	US-A-3 917 573 (G.G. PAREKH et al.) * Claims *	1-6	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 F C 08 K A 61 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 02-03-1989	Examiner MERGONI M.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	